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A Flux Ratio Theorem for Multicomponent Linear Diffusion Equations

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Abstract—Ussing [1] considered the steady flux of a single chemical component diffusing through a membrane under the influence of chemical potentials and derived from his linear model, an expression for the ratio of this flux and that of the complementary experiment in which the boundary conditions were interchanged. Here, an extension of Ussing's flux ratio theorem is obtained for n chemically interacting components governed by a linear system of diffusion-migration equations that may also incorporate linear temporary trapping reactions. The determinants of the output flux matrices for complementary experiments are shown to satisfy an Ussing flux ratio formula for steady state conditions of the same form as for the well-known one-component case.

Keywords—Diffusion, Flux, Flux ratio, Multicomponent.

1. INTRODUCTION

The flux ratio theory in [1] concerned with the ratio of the flux of a chemical component through a membrane, and the corresponding flux in a complementary experiment when the boundary conditions are reversed, has many extensions for linear systems concerned with the diffusion-migration of a single chemical component. His steady state constant flux ratio result was shown to hold for all time when the initial concentration of the diffusing chemical was zero, even under nonstationary boundary conditions [2] and when the process included temporarily trapping in the medium [3]. Some nonstationary results were also obtained for nonlinear transport models [4].

Some extensions for many interacting components were obtained by decoupling procedures with limited applicability [5], but numerical simulations demonstrate that for two or more chemically interacting components, in general such a result for any one flux component is no longer true.

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In this note, we show that Ussing's theorem can be extended to cover more general linear interacting systems involving many diffusing components by looking for a general linear mapping between the outfluxes of all the chemical components and the corresponding fluxes from the complementary experiments. We consider a linear system of diffusion-convection-reaction equations for the transport of n chemical components, which interact among themselves and with m trapped phases. The analysis here is restricted to one space dimension and may be considered a general linear model for chemical transport through a membrane.

2. TRANSPORT EQUATIONS

The linear diffusion-reaction equations on an interval $(0, L)$, considered here, model the transport through a membrane of thickness L of n chemical components interacting among themselves and with m trapped phases. At time t and position x in the membrane, the i^{th} chemical is at a concentration $c_i(x,t)$, has a local mass flux $j_i(x,t)$, and interacts with m trapped phases at concentrations $w_j(x,t)$. These concentrations and fluxes are assumed to be governed by linear diffusion-reaction equations of the form

$$\frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} = \sum_{j=1}^{n} a_{ij}(x)c_j + \sum_{l=1}^{m} b_{il}(x)w_l, \qquad 0 < x < L, \quad t > 0, \tag{2.1}$$

where the chemical fluxes are given by

$$j_i = -D_i(x)\frac{\partial c_i}{\partial x} + v_i(x)c_i, \tag{2.2}$$

and the linear trapping reactions governed by

$$\frac{\partial w_j}{\partial t} = \sum_{l=1}^{n} \alpha_{jl}(x)c_l + \sum_{k=1}^{m} \beta_{jk}(x)w_k. \tag{2.3}$$

The coefficients D_i, v_i, a_{ij}, b_{ij}, α_{ij}, β_{ij} are independent of time but may depend on x, and the diffusivities $D_i(x)$ are further restricted to be greater than zero everywhere.

At $t = 0$, the diffusing and trapped concentrations are given by $c_i = c_{0i}(x)$ and $w_j = w_{0j}(x)$ in $(0 < x < L)$ for all i and j, while on the boundaries of the membrane, $c_i(0,t) = f_i(t)$ and $c_i(L,t) = g_i(t)$ for $t > 0$.

3. LAPLACE TRANSFORM EQUATIONS

The Laplace transform $\bar{c}_i(x,p) \equiv \int_0^\infty e^{-pt}c_i(x,t)\,dt$ of $c_i(x,t)$ and the corresponding transforms of $w_j(x,t)$ and the fluxes $j_i(x,t)$ for the general linear system considered here satisfy the system of linear ordinary differential equations

$$\frac{d\bar{j}_i}{dx} = \sum_{j=1}^{n} a_{ij}(x)\bar{c}_j + \sum_{k=1}^{m} b_{ik}(x)\bar{w}_k - p\bar{c}_i + c_{0i}, \qquad 0 < x < L, \tag{3.1}$$

where

$$\bar{j}_i = -D_i(x)\frac{d\bar{c}_i}{dx} + v_i(x)\bar{c}_i, \tag{3.2}$$

$$p\bar{w}_j - w_{0j} = \sum_{l=1}^{n} \alpha_{jl}(x)\bar{c}_l + \sum_{k=1}^{m} \beta_{jk}(x)\bar{w}_k, \tag{3.3}$$

and boundary conditions

$$\bar{c}_i(o,p) = \bar{f}_i(p), \qquad \bar{c}_i(L,p) = \bar{g}_i(p). \tag{3.4}$$

This system can be expressed in matrix notation in the following form:

$$\frac{d\bar{\mathbf{j}}}{dx} = [\mathbf{a}(x) - p\mathbf{I}_n]\bar{\mathbf{c}} + \mathbf{b}(x)\bar{\mathbf{w}} + \mathbf{c}_0, \qquad 0 < x < L, \tag{3.5}$$

where

$$\bar{\mathbf{j}} = -\mathbf{D}(x)\frac{d\bar{\mathbf{c}}}{dx} + \mathbf{V}(x)\bar{\mathbf{c}}, \tag{3.6}$$

$$p\bar{\mathbf{w}} - \mathbf{w}_0 = \alpha(x)\bar{\mathbf{c}} + \beta(x)\bar{\mathbf{w}}, \qquad \text{so that } [p\mathbf{I}_m - \beta(x)]\bar{\mathbf{w}} = \mathbf{w}_0 + \alpha(x)\bar{\mathbf{c}}, \tag{3.7}$$

and

$$\bar{\mathbf{c}}(o,p) = \bar{\mathbf{f}}(p), \qquad \bar{\mathbf{c}}(L,p) = \bar{\mathbf{g}}(p), \tag{3.8}$$

where $\mathbf{a}$ is the $n \times n$ matrix of coefficients a_{ij}, $\mathbf{b}$ is the $n \times m$ matrix of coefficients b_{ij}, α is the $m \times n$ matrix of coefficients α_{ij}, β is the $m \times m$ matrix of coefficients β_{ij}, and $\mathbf{I}_m$ is the $m \times m$ unit matrix.

We are therefore able to construct a matrix system of $2n$ first-order differential equations of the form

$$\frac{d\bar{\mathbf{y}}}{dx} = \frac{d}{dx}\begin{bmatrix}\bar{\mathbf{c}}\\ \bar{\mathbf{j}}\end{bmatrix} = \begin{bmatrix}\mathbf{D}^{-1}(x)\mathbf{V}(x) & -\mathbf{D}^{-1}(x)\\ \mathbf{A}(x,p) & \mathbf{0}\end{bmatrix}\begin{bmatrix}\bar{\mathbf{c}}\\ \bar{\mathbf{j}}\end{bmatrix} + \begin{bmatrix}0\\ \mathbf{c}_0 + \mathbf{b}(x)[p\mathbf{I}_m - \beta]^{-1}\mathbf{w}_0\end{bmatrix}, \tag{3.9}$$

where

$$\mathbf{A}(x,p) = \mathbf{a}(x) - p\mathbf{I}_n + \mathbf{b}(x)(p\mathbf{I}_m - \beta)^{-1}\alpha(x), \tag{3.10}$$

and so

$$\frac{d\bar{\mathbf{y}}}{dx} = \mathbf{B}(x,p)\bar{\mathbf{y}} + \bar{\mathbf{z}}_0(x,p), \tag{3.11}$$

where

$$\mathbf{B}(x,p) = \begin{bmatrix}\mathbf{D}^{-1}(x)\mathbf{V}(x) & -\mathbf{D}^{-1}(x)\\ \mathbf{A}(x,p) & \mathbf{0}\end{bmatrix} \quad \text{and} \quad \bar{\mathbf{z}}_0(x,p) = \begin{bmatrix}0\\ \mathbf{c}_0 + \mathbf{b}(x)[p\mathbf{I}_m - \beta]^{-1}\mathbf{w}_0\end{bmatrix}. \tag{3.12}$$

Thus, the Laplace transform of a $2n \times 2n$ matrix $\mathbf{Y}$ representing $2n$ vector solutions satisfies a linear matrix differential equation of the form

$$\frac{d\bar{\mathbf{Y}}}{dx} = \mathbf{B}(x,p)\bar{\mathbf{Y}} + \mathbf{Z}_0(x,p), \tag{3.13}$$

where

$$\bar{\mathbf{Y}} = \begin{bmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{bmatrix}, \quad \mathbf{B}(x,p) = \begin{bmatrix}\mathbf{D}^{-1}(x)\mathbf{V}(x) & -\mathbf{D}^{-1}(x)\\ \mathbf{A}(x,p) & \mathbf{0}\end{bmatrix}, \quad \mathbf{Z}_0(x,p) = \begin{bmatrix}0 & 0\\ \mathbf{Z}_{01} & \mathbf{Z}_{02}\end{bmatrix}, \tag{3.14}$$

$$\mathbf{Z}_{01} = \mathbf{c}_{01} + \mathbf{b}(x)[p\mathbf{I}_m - \beta]^{-1}\mathbf{w}_{01}, \qquad \text{and} \qquad \mathbf{Z}_{02} = \mathbf{c}_{02} + \mathbf{b}(x)[p\mathbf{I}_m - \beta]^{-1}\mathbf{w}_{02}, \tag{3.15}$$

and

$$\bar{\mathbf{Y}}(0,p) = \begin{bmatrix}\bar{\mathbf{F}}_1 & \bar{\mathbf{F}}_2\\ \bar{\mathbf{J}}_{10} & \bar{\mathbf{J}}_{20}\end{bmatrix}, \qquad \bar{\mathbf{Y}}(L,p) = \begin{bmatrix}\bar{\mathbf{G}}_1 & \bar{\mathbf{G}}_2\\ \bar{\mathbf{J}}_{1L} & \bar{\mathbf{J}}_{2L}\end{bmatrix}. \tag{3.16}$$

4. FLUX RATIO THEOREM

If $\mathbf{S}(x)$ is a nonsingular $2n \times 2n$ matrix with differentiable coefficients, then the derivative of its determinant Θ is the sum of n determinants obtained by differentiating each row of Θ in turn. These n determinants form the diagonal elements of $\frac{d\mathbf{S}}{dx} \cdot \operatorname{adj}\mathbf{S}$, and so the derivative of Θ satisfies the differential equation

$$\frac{d\Theta}{dx} = \operatorname{tr}\left(\frac{d\mathbf{S}}{dx} \cdot \operatorname{adj}\mathbf{S}\right) = \operatorname{tr}\left(\frac{d\mathbf{S}}{dx} \cdot \mathbf{S}^{-1}\right)\Theta. \tag{4.1}$$

Equation (3.13) and the determinant derivative formula (4.1) therefore give rise to the differential equation

$$\frac{d}{dx}\begin{vmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{vmatrix} = \operatorname{tr}\left(\begin{bmatrix}\mathbf{D}^{-1}(x)\mathbf{V}(x) & -\mathbf{D}^{-1}(x)\\ \mathbf{A}(x,p) & \mathbf{0}\end{bmatrix} + \begin{bmatrix}0 & 0\\ \mathbf{Z}_{01} & \mathbf{Z}_{02}\end{bmatrix}\begin{bmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{bmatrix}^{-1}\right)\begin{vmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{vmatrix}, \tag{4.2}$$

for the determinant of $\bar{\mathbf{Y}}$, and if we write

$$f(x,p) = \operatorname{tr}\left(\begin{bmatrix}\mathbf{D}^{-1}(x)\mathbf{V}(x) & -\mathbf{D}^{-1}(x)\\ \mathbf{A}(x,p) & \mathbf{0}\end{bmatrix} + \begin{bmatrix}0 & 0\\ \mathbf{Z}_{01} & \mathbf{Z}_{02}\end{bmatrix}\begin{bmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{bmatrix}^{-1}\right), \tag{4.3}$$

and integrate the differential equation (4.2) from 0 to L, we are led to the expression

$$\begin{vmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{vmatrix}(L,p) = e^{\int_0^L f(x,p)\,dx}\begin{vmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{vmatrix}(0,p). \tag{4.4}$$

Suppose the first set of n experiments satisfies the boundary conditions

$$\bar{\mathbf{C}}_1(0,p) = \bar{\mathbf{C}}_1^0(p), \qquad \bar{\mathbf{C}}_1(L,p) = 0, \tag{4.5}$$

while the second set of n experiments satisfies the complementary boundary conditions

$$\bar{\mathbf{C}}_2(0,p) = 0, \qquad \bar{\mathbf{C}}_2(L,p) = \bar{\mathbf{C}}_2^L(p).$$

Equation (4.4) then gives the flux transform expression

$$-\left|\mathbf{C}_2^L(p)\right|\left|\bar{\mathbf{J}}_1(L,p)\right| = e^{\int_0^L f(x,p)\,dx}\left|\mathbf{C}_1^0(p)\right|\left|\bar{\mathbf{J}}_2(0,p)\right|. \tag{4.6}$$

If $\mathbf{Z}_{01}$ and $\mathbf{Z}_{02}$ arise from steady state distributions, we can write

$$\mathbf{Z}_{01} = \mathbf{K}(x,p)\mathbf{C}_{01}, \qquad \text{and} \qquad \mathbf{Z}_{02} = \mathbf{K}(x,p)\mathbf{C}_{02}, \tag{4.7}$$

where

$$\mathbf{K}(x,p) = \left\{\mathbf{I}_n - \mathbf{b}(x)\left[p\beta - \beta^2\right]^{-1}\alpha\right\} = \frac{[\mathbf{A}(x,0) - \mathbf{A}(x,p)]}{p}, \tag{4.8}$$

so that equation (4.3) becomes

$$f(x,p) = \operatorname{tr}\left(\mathbf{D}^{-1}(x)\mathbf{V}(x)\right) + \operatorname{tr}\left(\begin{bmatrix}0 & 0\\ \mathbf{K}(x,p) & 0\end{bmatrix}\begin{bmatrix}\mathbf{C}_{01} & \mathbf{C}_{02}\\ \mathbf{J}_{01} & \mathbf{J}_{02}\end{bmatrix}\begin{bmatrix}\bar{\mathbf{C}}_1 & \bar{\mathbf{C}}_2\\ \bar{\mathbf{J}}_1 & \bar{\mathbf{J}}_2\end{bmatrix}^{-1}\right). \tag{4.9}$$

In the cases where the initial concentrations $\mathbf{C}_{01}$ and $\mathbf{C}_{02}$ are zero, or are all steady state solutions so that

$$\bar{\mathbf{C}}_1 = \frac{\mathbf{C}_{01}}{p}, \quad \bar{\mathbf{J}}_1 = \frac{\mathbf{J}_{01}}{p} \qquad \text{and} \qquad \bar{\mathbf{C}}_2 = \frac{\mathbf{C}_{02}}{p}, \quad \bar{\mathbf{J}}_2 = \frac{\mathbf{J}_{02}}{p}, \tag{4.10}$$

the second term in the trace expression (4.9) is zero so that

$$f(x) = \operatorname{tr}\left(\mathbf{D}^{-1}(x)\mathbf{V}(x)\right), \tag{4.11}$$

and is independent of p.

We have here a generalized flux ratio result of the form

$$-\left|\bar{\mathbf{J}}_1\right|(L,p) = e^{\int_0^L \operatorname{tr}\left(\mathbf{D}^{-1}(x)\mathbf{V}(x)\right)dx}\left|\bar{\mathbf{J}}_2\right|(0,p), \tag{4.12}$$

for cases where the initial concentrations $\mathbf{C}_{01}$ and $\mathbf{C}_{02}$ are zero, or are all steady state solutions and the boundary concentration matrices $|\mathbf{C}_1^0(p)|$ and $|\mathbf{C}_2^L(p)|$ have been chosen equally.

For the case $n = 1$ involving just one diffusing chemical, the determinants consist of one element and the transforms can be inverted on both sides to give the well-known Ussing flux ratio result

$$-\mathbf{J}_1(L,t) = e^{\int_0^L \operatorname{tr}\left(\mathbf{D}^{-1}(x)\mathbf{V}(x)\right)dx}\mathbf{J}_2(0,t). \tag{4.13}$$

In cases where $f(x)$ is independent of p, the transform expression may be inverted with each side written as a sum of multiple convolutions. For n greater than one and all solutions being steady state solutions, the transforms on each side of equation (4.12) may also be inverted to give

$$-|\mathbf{J}_1|(L) = e^{\int_0^L \operatorname{tr}\left(\mathbf{D}^{-1}(x)\mathbf{V}(x)\right)dx}|\mathbf{J}_2|(0). \tag{4.14}$$

If the first $n-1$ experiments and their complementary counterparts generating the first $n-1$ columns of $\mathbf{J}_1$ and $\mathbf{J}_2$ are taken as fixed, then equation (4.14) defines a fixed linear relationship between the n components of the outfluxes and their complementary counterparts for the n^{th} experiment.

5. STEADY STATE COMPLEMENTARY EXPERIMENTS

The general determinantal relationship for steady state solutions of equation (3.13) is

$$\begin{vmatrix} \mathbf{C}_1 & \mathbf{C}_2 \\ \mathbf{J}_1 & \mathbf{J}_2 \end{vmatrix}(L) = e^{\int_0^L f(x)\,dx} \begin{vmatrix} \mathbf{C}_1 & \mathbf{C}_2 \\ \mathbf{J}_1 & \mathbf{J}_2 \end{vmatrix}(0), \tag{5.1}$$

where $f(x)$ is given by (4.11). There are four $n \times n$ matrices involved in each of these two determinants, and in the last section we considered complementary experiments in which the concentrations at the two boundaries governed the play. When two or more interacting components are involved, it is worth considering some alternative experimental approaches.

Consider zero flux boundary conditions. In the first experiment, $\mathbf{C}_1(0)$ is prescribed and at $x = L$ a flux barrier establishes a zero flux condition $\mathbf{J}_1(L) = 0$ at $x = L$ but allows $\mathbf{C}_1(L)$ to be measured by sampling a boundary layer there when equilibrium has been reached. In general, $\mathbf{J}_1(0)$ will not be zero for all components unless $\mathbf{C}_1(0)$ is an equilibrium distribution of concentrations. In this case, for passive membranes, we finally establish a steady state zero flux state, but in general there will be only m of these independent states where $m < n$ depending on the rank of the reaction matrix at $x = 0$. In the second complementary set of experiments, the zero flux condition is established at the opposite boundary while concentrations $\mathbf{C}_2(L)$ are maintained at $x = L$ until equilibrium is established and a steady state concentration matrix $\mathbf{C}_2(0)$ has been measured. For such a set of experiments, our determinant equation gives

$$\begin{vmatrix} \mathbf{C}_1 & \mathbf{C}_2 \\ \mathbf{0} & \mathbf{J}_2 \end{vmatrix}(L) = e^{\int_0^L f(x)\,dx} \begin{vmatrix} \mathbf{C}_1 & \mathbf{C}_2 \\ \mathbf{J}_1 & \mathbf{0} \end{vmatrix}(0), \tag{5.2}$$

so that

$$|\mathbf{C}_1(L)|\,|\mathbf{J}_2(L)| = -e^{\int_0^L f(x)\,dx}|\mathbf{C}_2(0)|\,|\mathbf{J}_1(0)|, \tag{5.3}$$

and if the complementary concentrations are taken as equal, we have a flux ratio expression

$$|\mathbf{J}_2(L)| = -e^{\int_0^L f(x)\,dx}|\mathbf{J}_1(0)| \tag{5.4}$$

for the input boundary.

Alternatively, we might consider establishing a given input matrix $\mathbf{J}_1(0)$ at $x = 0$ while maintaining zero concentrations at $x = L$, and at equilibrium we measure the output flux $\mathbf{J}_1(L)$ and the input concentrations $\mathbf{C}_1(0)$. In the complementary experiments, these conditions are reversed and our determinant gives

$$|\mathbf{C}_2(L)|\,|\mathbf{J}_1(L)| = -e^{\int_0^L f(x)\,dx}|\mathbf{C}_1(0)|\,|\mathbf{J}_2(0)|. \tag{5.5}$$

6. AN EXAMPLE

We consider here a general nonlinear system involving three diffusing interacting components of the form

$$\frac{\partial c_i}{\partial t} + \frac{\partial j_i}{\partial x} = r_i\left(\mathbf{x}, c_j, w_k\right), \qquad 0 < x < L, \quad t > 0, \tag{6.1}$$

as a model for a passive membrane, where the chemical fluxes are given by

$$j_i = -D_i\left(x, c_j, w_k\right)\frac{\partial c_i}{\partial x} + v_i\left(x, c_j, w_k\right)c_i, \tag{6.2}$$

and the trapping reactions are governed by

$$\frac{\partial w_j}{\partial t} = \rho_j\left(x, c_j, w_k\right). \tag{6.3}$$

This system is first brought to a steady, zero flux state $c_i = C_i(x)$, $w_j = W_j(x)$, $j_i = 0$ by equilibrium boundary conditions $c_i(o,t) = C_i^0$ at $\mathbf{x} = 0$ and $c_i(L,t) = C_i^L$ at $x = L$, established by a zero flux condition there. In this state,

$$D_i\left(x, C_j(x), W_k(x)\right)\frac{\partial C_i}{\partial x} - v_i\left(x, C_j(x), W_k(x)\right)C_i = D_i(x)\frac{\partial C_i}{\partial x} - v_i(x)C_i = 0, \tag{6.4}$$

and so

$$C_i^L = e^{\int_0^L D_i^{-1}(x)v_i(x)\,dx}C_i^0. \tag{6.5}$$

The flux experiment starts from this state by substituting for C_1^0 a mixture of c_1 and a radioactively tagged variant of it, c_1^*, so that the mixture is at the same chemical potential as the original untagged solution. If the chemistry, chemical kinetics, and transport properties are unaffected by the radioactive tagging, and the reactions are of the form

$$c_1 + c_2 \Leftrightarrow c_3, \qquad c_i \Leftrightarrow w_i, \tag{6.6}$$

with rates given by

$$r_1 = -k_1c_1c_2 + k_2c_3, \quad r_2 = r_1 = -r_3, \quad \rho_j = -c_j\left(N_j - m_jw_j\right) + K_jw_j, \tag{6.7}$$

then the components c_1^* and c_3^* diffuse and interact with w_1^* and w_3^* in a manner governed by the linear equations

$$\begin{aligned} \frac{\partial c_1^*}{\partial t} + \frac{\partial j_1^*}{\partial x} &= r_1^* = -k_1C_2(x)c_1^* + k_2c_3^*, \qquad 0 < x < L, \quad t > 0, \\ \frac{\partial c_3^*}{\partial t} + \frac{\partial j_3^*}{\partial x} &= r_3^* = k_1C_2(x)c_1^* - k_2c_3^*, \qquad 0 < x < L, \quad t > 0, \end{aligned} \tag{6.8}$$

where the fluxes are given by

$$j_i^* = -D_i\left(x, C_j(x), W_k(x)\right)\frac{\partial c_i^*}{\partial x} + v_i\left(x, C_j(x), W_k(x)\right)c_i^* = -D_i(x)\frac{\partial c_i^*}{\partial x} + v_i(x)c_i^*, \tag{6.9}$$

and trapping kinetics given by

$$\frac{\partial w_j^*}{\partial t} = -c_j^*\left(N_j - m_jW_j(x)\right) + K_jw_j^*. \tag{6.10}$$

The final steady state radioactive flux is governed by the linear equations

$$\begin{aligned} \frac{\partial j_1^*}{\partial x} &= r_1^* = -k_1C_2(x)c_1^* + k_2c_3^*, \qquad 0 < x < L, \\ \frac{\partial j_3^*}{\partial x} &= r_3^* = k_1C_2(x)c_1^* - k_2c_3^*, \qquad 0 < x < L, \end{aligned} \tag{6.11}$$

where the fluxes are given by

$$j_i^* = -D_i(x)\frac{\partial c_i^*}{\partial x} + v_i(x)c_i^*, \tag{6.12}$$

and the radioactive trapping concentrations are given by

$$w_j^* = c_j^*\frac{(N_j - m_j W_j(x))}{K_j}. \tag{6.13}$$

The determinant flux equation (4.6) for steady state solutions gives the following equation:

$$-\begin{vmatrix} c_{1,1}^{*c} & c_{2,1}^{*c} \\ c_{1,3}^{*c} & c_{2,3}^{*c} \end{vmatrix}(L)\begin{vmatrix} j_{1,1}^* & j_{2,1}^* \\ j_{1,3}^* & j_{2,3}^* \end{vmatrix}(L) = e^{\int_0^L \operatorname{tr}\left(\mathbf{D}^{-1}(x)\mathbf{V}(x)\right)dx}\begin{vmatrix} c_{1,1}^* & c_{2,1}^* \\ c_{1,3}^* & c_{2,3}^* \end{vmatrix}(0)\begin{vmatrix} j_{1,1}^{*c} & j_{2,1}^{*c} \\ j_{1,3}^{*c} & j_{2,3}^{*c} \end{vmatrix}(0), \tag{6.14}$$

where $c_{1,i}^*, j_{1,i}^*, c_{2,i}^*, j_{2,i}^*$ are the boundary concentrations and fluxes for a pair of steady state experiments producing radioisotope outputs at L in the first experiment, and $c_{1,i}^{*c}, j_{1,i}^{*c}, c_{2,i}^{*c}, j_{2,i}^{*c}$ are the corresponding boundary concentrations and fluxes in the complementary experiment.

Now suppose, in the first experiment, the radioactive concentrations $c_{1,1}^*$ and $c_{1,3}^*$ are assumed to be in equilibrium at the boundary $x = 0$. Such a boundary condition maintained together with a no flux condition at $x = L$ would establish a steady state, zero flux distribution throughout the membrane for both the tagged and untagged components, and if the fraction of radioisotope at the boundary were maintained constant at the value α, say, for component one, it would establish the same fraction of radioactively tagged components throughout the membrane for all the components. In this state, we have

$$c_{1,i}^*(x) = \alpha C_i(x). \tag{6.15}$$

If the complementary experiment were set up with boundary conditions $c_{1,i}^{*c}(L) = \alpha C_i(L)$ at $x = L$, then the fluxes $j_{1,i}^{*c}$ would be just $-j_{1,i}^*$, since the superposition of these two solutions is a steady state zero flux solution. By choosing our first experiment and its complement in this way using one of the one parameter set with equilibrium boundary conditions at $x = 0$ of the form (5.15), then steady state output fluxes of any second experiment with nonequilibrium boundary conditions such as, say,

$$c_{2,1}^*(0) = \beta C_1(0), \qquad c_{2,3}^*(0) = 0, \qquad c_{2,1}^{*c}(L) = \beta C_1(L), \qquad c_{2,3}^{*c}(L) = 0, \tag{6.16}$$

which fall outside the one parameter set of equilibrium boundary conditions, satisfy the linear equation

$$-\begin{vmatrix} \alpha C_1^L & \beta C_1^L \\ \alpha C_2^L & 0 \end{vmatrix} \times \begin{vmatrix} j_{1,1}^* & j_{2,1}^* \\ j_{1,3}^* & j_{2,3}^* \end{vmatrix}(L) = e^{\int_0^L \operatorname{tr}\left(\mathbf{D}^{-1}(x)\mathbf{V}(x)\right)dx}\begin{vmatrix} \alpha C_1^0 & \beta C_1^0 \\ \alpha C_3^0 & 0 \end{vmatrix} \times \begin{vmatrix} -j_{1,1}^* & j_{2,1}^{*c} \\ -j_{1,3}^* & j_{2,3}^{*c} \end{vmatrix}(0) \tag{6.17}$$

or

$$\begin{vmatrix} j_{1,1}^* & j_{2,1}^* \\ j_{1,3}^* & j_{2,3}^* \end{vmatrix}(L) = \begin{vmatrix} j_{1,1}^* & j_{2,1}^{*c} \\ j_{1,3}^* & j_{2,3}^{*c} \end{vmatrix}(0). \tag{6.18}$$

This result extends Ussing's flux ratio result to cases involving many chemically interacting components, and the radioisotope technique allows for applications to nonlinear systems of very general form. The many published extensions of the Ussing result to transient flux ratios just slip through the net in this treatment, but some interesting special cases can be recovered and will be treated in a later paper.

REFERENCES

1. H.H. Ussing, Interpretation of tracer fluxes, In *Membrane Transport in Biology, Vol. 1*, (Edited by G. Giebisch *et al.*), pp. 115–140, Springer, New York, (1978).
2. L. Bass and A.J. Bracken, The flux ratio equation under nonstationary boundary conditions, *Mathematical Biosciences* **66**, 87–92, (1983).
3. L. Bass, A.J. Bracken and J. Hilden, Flux ratio theorems for nonstationary membrane transport with temporary capture of tracer, *J. Theor. Biol.* **118**, 327–338, (1986).
4. L. Bass and A. McNabb, Flux ratio theorems for nonlinear membrane transport under nonstationary boundary conditions, *J. Theor. Biol.* **133**, 185–191, (1988).
5. A. McNabb and L. Bass, Flux theorems for linear multicomponent diffusion, *IMA Journal of Applied Mathematics* **44**, 155–161, (1990).